Chemistry

M. I. Yanovskii and G. A. Gaziev

1958

SovietRxiv

Figure 1: Frontal breakthrough curves of hydrocarbon gases.

Figure 1: Figure 1: Frontal breakthrough curves of hydrocarbon gases.

Abstract

Full Text

Chemistry

M. I. Yanovskii and G. A. Gaziev

APPLICATION OF FRONTAL ANALYSIS IN GAS-LIQUID CHROMATOGRAPHY OF RADIOACTIVE AND NONRADIOACTIVE GASES

(Presented by Academician S. I. Volľ fkovich, January 2, 1958)

Gas-adsorption frontal analysis has not found wide application in analytical practice because, in this method, the dynamics of adsorption in the adsorbent layer is considerably complicated by displacement processes associated with the mutual influence of the components of the mixture during their absorption on the surface ($^{1-3}$), as a result of which the composition of the mixture cannot be determined directly from the frontal diagram. Calculations require exhaustive data on the adsorption isotherms of mixtures and of individual components over the entire concentration range under study. The insufficient development of the theory of adsorption of mixtures under static and dynamic conditions, and the insufficiency of experimental materials in this field, limit the application of adsorption frontal analysis to a narrow range of systems obeying Langmuir-type adsorption equations (^{2,3}).

Fig. 1. Frontal breakthrough curves of hydrocarbon gases.
a –0.98% C_3H_6 in hydrogen; *b* –0.98% C_3H_6 and 1.03% C_4H_6; *c* –0.98% C_3H_6, 1.03% C_4H_6, and 2.93% n-C_6H_{14}.

In the present work an attempt has been made to apply frontal analysis in gas-liquid chromatography, the displacement variant of which became widely used after the well-known works of James and Martin (^{4}).

As is known, in gas-liquid chromatography, under certain conditions (low concentrations, weak solubility of the gas in the liquid), one may neglect the difference between the solubility of a gas from a mixture and the solubility of the pure gas. This circumstance, due to the absence of mutual influence of the components in the gas and liquid phases, greatly simplifies frontal analysis and makes it possible to determine the composition of the analyzed mixture without resorting to preliminary measurements and calculations—directly from the frontal diagram.

The experiment consisted in the continuous passage of the analyzed mixture of substances through a column and in recording the so-called frontal diagram, which characterizes the relationship between the concentration of components at the outlet of the column and the volume of the mixture passed through it. The principal elements of the experimental setup were a gas–liquid chromatographic column filled with a specially treated inert carrier.

tel (diatomite), impregnated with a high-boiling liquid (nitrobenzene, dibutyl phthalate, etc.), and a thermoconductometric gas analyzer with a self-recording potentiometer EPP-09.

Fig. 2. Frontal (a) and displacement (b) gas–liquid analysis of multicomponent mixtures

Some frontal diagrams obtained on a gas–liquid column are shown in Fig. 1 (diatomite + dibutyl phthalate; length 1.65 m, $d = 5$ mm; purge rate 7 ml/min). They indicate that, to a first approximation, the mutual influence of the components in the stationary phase may be neglected: the beginning of the C_3H_6 step and its height, corresponding to one and the same propylene content (0.98%), are identical in all three diagrams, despite the addition of divinyl and hexane. Hexane, in turn, has no effect on the height of the divinyl step (cf. Fig. 1b and 1c).

Fig. 2 illustrates the possibility of analyzing an eight-component mixture (diatomite + nitrobenzene; length 16 m, $d = 5$ mm; purge rate 7 ml/min). Fig. 2b gives a displacement gas–liquid chromatogram of 50 cm^3 of a mixture of the same composition as in the experiment presented in Fig. 2a, under identical process parameters (column length, carrier-gas flow rate, detection sensitivity). Comparison of Figs. 2a and 2b shows that each step in the frontal diagram corresponds to a displacement peak.

Frontal gas–liquid analysis may be used, along with the radiochromatographic displacement variant (^{5}), for the rapid determination of the specific radioactivity of the components of a gas mixture. For this purpose, parallel to (or in series with) the conductometric gas analyzer, the gas stream is passed through a radiometric cell, the design of which has been described previously (^{6}). The radiometric cell, in which thin-walled end-window counters are mounted and connected in parallel to the integrating circuit of the count-rate meter, makes it possible to determine the radioactivity of the gas stream at the outlet of the column. The readings of the radiometric cell are recorded simultaneously with the readings of the thermoconductometric gas analyzer on one strip of the recorder.

A typical frontal gas–liquid radiochromatogram of a mixture of air, propylene, divinyl, and pentane in hydrogen is shown in Fig. 3,

(diatomite + dibutyl phthalate; column length 1.65 m, $d = 5$ mm; gas flow rate

Fig. 3

Figure 2: Fig. 3

Fig. 4

Figure 3: Fig. 4

7 ml/min). It shows that only two of the four components (C_3H_6 and C_4H_6) are radioactive, since only for the propylene and divinyl steps on curve *a* are there corresponding steps on curve *b*. The specific radioactivity of component $I_{\mathrm{sp}i}$ is readily determined as the ratio of the step height ΔI_i on curve *b* to the step height ΔC_i on curve *a*:

$$I_{\mathrm{sp}i} = \frac{\Delta I_i}{\Delta C_i},$$

taken in definite scales. After the analysis is completed, when no further new steps are recorded on the frontal diagram, the column is subjected to desorption by passing the carrier gas (H_2) through it at the same rate until a stable zero position is reached. This purging process can be used to obtain a desorption frontal diagram, from which the composition of the mixture is sometimes also determined. In Fig. 4, the solid line $ABCDE$ shows the frontal diagram of a mixture of propylene and divinyl. At point E, corresponding to the moment when the supply of the C_3H_6 and C_4H_6 mixture to the column was stopped, the column began to be purged with hydrogen. The resulting desorption curve $A'B'C'D'E'$ is completely identical to the frontal diagram $ABCDE$ and can be superposed on it if the curve $EA'B'C'D'$ is shifted to point O, aligning the v axis with the v' axis. The shifted desorption curve $A''B''C''D''E''$ is a mirror image of the frontal diagram $ABCDE$. After completion of the desorption experiment, the column is again ready for recording a chromatogram.

Fig. 3. Frontal gas-liquid radiochromatogram. *a*—record of the readings of the thermoconductometric gas analyzer; *b*—record of the readings of the radiometric cell

Fig. 4. Absorption and desorption frontal diagrams of a mixture of propylene and divinyl

Received
31 XII 1957

REFERENCES CITED

1. M. M. Dubinin, S. Yavich, ZhPKh, **9**, 1191 (1936).

2. O. M. Todes, ZhPKh, **18**, 591 (1945).
3. S. Klasson, *Adsorption Analysis of Mixtures*, 1950.
4. A. T. James, A. J. P. Martin, *Biochem. J.*, **56**, 679 (1952).
5. M. I. Yanovskii, D. S. Kapustin, V. A. Nogotkov-Ryutin, in: *Collected Papers: Isotopes in Catalysis*, **9**, 1957.
6. M. I. Yanovskii, *Radiochromatograph*, *Instruments and Stands*, Moscow, 1958.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.